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USE OF BINARY ALLOYS OF THE LANTHANIDES FOR TRITIUM RECOVERY FROM CTR BLANKETS*

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Liquid binary alloys of the lanthanide metals have been proposed as getters of tritium from breeder blankets of controlled thermonuclear reactors. Because of the high stability of the lanthanide hydrides at reactor temperatures (500-1000°C), these alloys should prove highly efficient in this application and a series of experiments designed to test this applicability are summarized here. Sieverts' experiments using deuterium were carried out on a series of alloys of La and Ce. For eutectics of the approximate composition Ln_5M where Ln is La or Ce and M is an iron-group metal, it was found that the deuteriding capacities and the equilibrium pressures were close to those of the parent metal. Experiments measuring the extraction rate of low-level tritium from helium streams using $La_{5.25}Ni$ were carried out. The tritium was rapidly gettered down to about 10 ppm and more slowly over periods of 1-2 h to below 0.1 ppm.

INTRODUCTION

Low-melting eutectic alloys of the lanthanide metals could prove useful as extractors of tritium from breeder blankets of controlled thermonuclear reactors (CTRs). Their prime application seems to be in those designs which employ helium-cooled, solid lithium blankets where they serve to scrub the tritium from the circulating helium streams. However, if the mutual solubilities of the alloys and lithium are not too great, they could also be used in liquid lithium-blanket applications as liquid-liquid extractors. Numerous examples of eutectic alloys have been reported in the literature[1] consisting primarily of La, Ce, or Pr coupled with metals such as Au, Ag, Cu, Fe, Co, or Ni. Typical melting points are 400-800°C. Undoubtedly many other combinations produce eutectics with appropriate characteristics. Because of the potentially large number of alloys it should be possible to choose an appropriate getter based on such physical properties as mutual solubilities, equilibrium pressures, melting points, and chemical properties.

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Experiments designed to evaluate promising eutectic alloys are summarized here. Initial experiments on the hydriding characteristics were done with D_2 and several alloys of Ce[2] and La.[3] In addition, experiments using the getter $La_{5.25}Ni$ and tritium have been performed.[4]

SIEVERTS' EXPERIMENTS WITH DEUTERIUM

One of the first objectives of this study was to establish the general hydriding characteristics of the alloys. To this end Sieverts' experiments (measurements of equilibrium pressure versus composition at constant temperature) were done on a number of alloys of Ce and La.

Results for Ce metal and several of its eutectic alloys are shown in Figure 1. Lanthanide metals[5,6] typically display a region of constant pressure in the pressure versus composition diagram. This plateau generally begins at $H/Ln \simeq 0.2$ and crosses to $H/Ln \simeq 2$ at which point the pressure rises sharply. The constant pressure plateau is a result of the coexistance of the two phases Ln and LnH_2. As can be seen in the figure, similar results were observed for Ce and all the alloys studied, although the

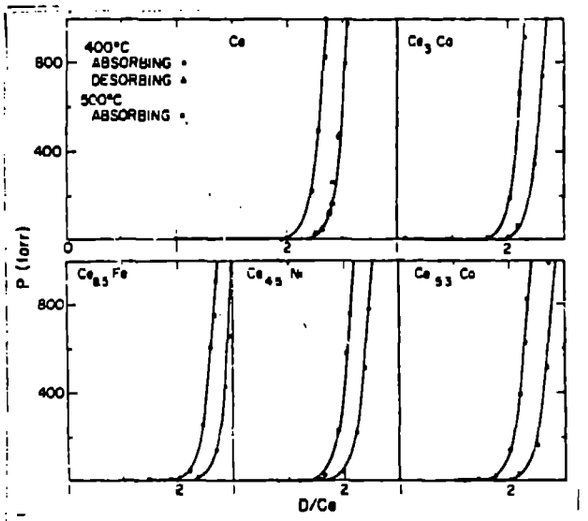

FIGURE 1. Absorption isotherms of Ce and its alloys at 400 and 500°C.

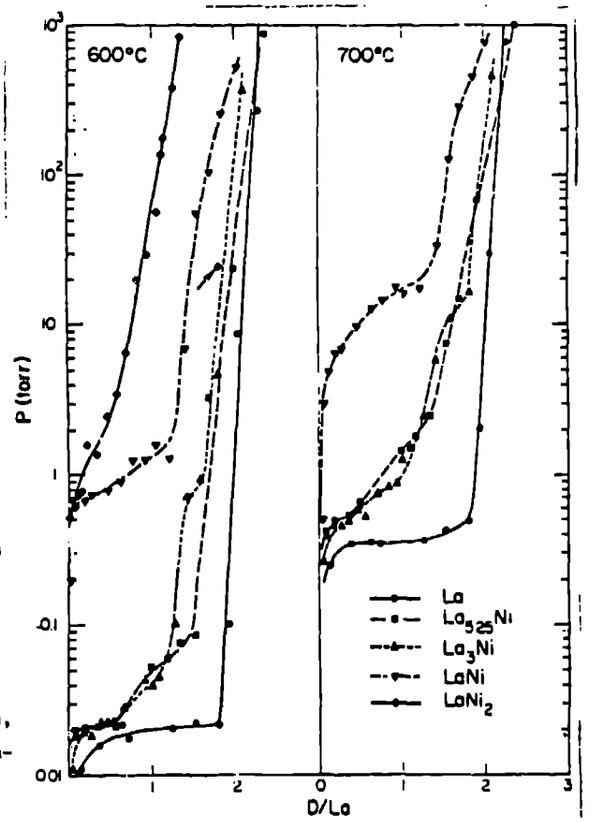

FIGURE 2. Absorption isotherms of La and its alloys at 600-700°C.

plateau is not evident in the figure because of its low value. The only significant difference between the metal and the various alloys is the change in absorption capacity, defined by the rise in pressure, which is decreased by 10-20% in the alloys. This decrease can be explained by the formation of stable intermediate compounds (CeM, CeM_2, etc.) which are unreactive to deuterium under the experimental conditions.[2]

Similar results were observed for a series of La-Ni alloys, shown in Figure 2. In this case a more detailed study of the pressure versus composition diagram was made. The important results found are as follows. (1) Equilibrium pressures increase as the Ni content increases in the alloys. (2) Adsorption capacity decreases in the same direction. (3) New plateaus, apparently coming from the separation of other La-Ni-D phases, are seen. For this system the unreacting stable compound appears to be $LaNi_5$.[3]

For all the Ce and La species studied the variation of pressure with temperature in the center of the plateau region (D/Ln = 1) was studied and in all cases linear in P versus 1/T dependence was observed. These results are tabulated below giving values of A and B for the relationship ln P (torr) = -A/T + B for all. Heats (ΔH) and entropies (ΔS) of reaction, calculated from these constants, and the reported melting points[1] are also given.

Species	$Ax10^{-3}$	B	-ΔH (kcal mole D_2)	-ΔS (eu mole D_2)	M.P. (°C)
Ce	23.0	22.5	46	31	820
Ce_3Co	28.1	29.3	56	45	470
$Ce_{5.3}Co$	26.1	26.7	52	40	435
$Ce_{4.5}Ni$	32.3	34.3	64	55	470
$Ce_{8.5}Fe$	27.3	27.3	54	41	680
La	25.5	26	51	38	812
$La_{5.25}Ni$	27	27	54	40	495
La_3Ni	26	30	53	46	515
LaNi	21	25	42	36	685

Data from this table can be used as a means of evaluating various alloys as getters. Note that the plateau pressure as calculated from the above equation is an upper bound for the pressure in CTR

operation, since in this application they will be operated at low concentrations. In addition to a low equilibrium pressure, another desirable quality in a getter is a high ΔH. This arises from the necessity of regenerating the loaded getter, done by heating the alloy and driving off the tritium. The more negative ΔH, the greater the change in pressure with temperature and the easier it would be to regenerate.

TRITIUM GETTERING

A series of experiments measuring the absorption of tritium from a helium stream using the eutectic $La_{5.25}Ni$ was done. The apparatus, constructed of 300-series stainless steel (except for Teflon seals in the valves and a copper gasket in the furnace), is shown in Figure 3. The molten sample was held in a tungsten or stainless steel crucible placed in the externally heated, internally gold-plated, furnace. The helium gas was circulated around the apparatus with a metal bellows pump at rates of 120-140 cc/sec. Tritium was stored on a uranium bed as UT_3. The standard volume was used to increase the capacity of the system and during absorption runs the valves were adjusted such that roughly half the flow passed through the volume, half through the furnace. The concentration of tritium in the gas was continuously monitored with a mass spectrometer which was periodically calibrated with prepared gas mixes (see reference 4 for details).

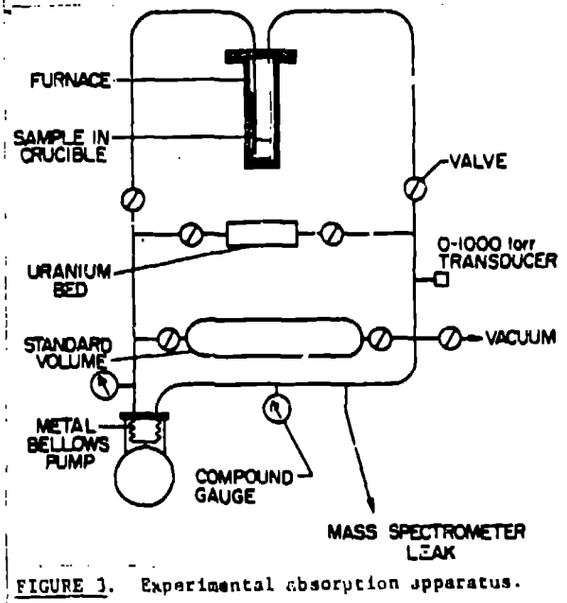

FIGURE 1. Experimental absorption apparatus.

The general experimental technique was as follows. A quantity of the alloy was broken up, weighed, and placed in the furnace, which was then sealed. After the furnace was connected to the circulation manifold, the entire system was filled to roughly 600 torr with helium gas. The furnace was then heated, and simultaneously, the uranium bed was brought up to the desired temperature. With the sample furnace valved off from the system, tritium was added to the circulating gas until the required pressure had been achieved, usually about 10 torr. After the signal became constant, the bed was valved off and the valves to the furnace opened, and, the drop in tritium pressure was then monitored with the spectrometer. Every third or fourth addition was for more highly concentrated mixes (20%), which were carefully prepared and measured with the pressure transducer. These mixes were used to recalibrate the spectrometer response as well as to check out the kinetics of absorption of large amounts of tritium.

In these measurements two main runs were made, each consisting of several successive additions of tritium to the melt. In the first run eight tritium additions were made, including six low-level additions (10 torr tritium) and two high (100 torr tritium), all at 600°C. The results are plotted on a log scale in Figure 4, which shows the decrease in pressure of tritium with time. In the figure n refers to the tritium-to-lanthanum ratio in the final product of each addition. Several general results can be deduced from the figure: (1) At low concentrations and for low-level additions, the alloy is capable of getter ng to the ppm range over short periods. (2) For low concentrations of tritium the half-life of absorption is on the order of about 20 s. Experiments with the uranium bed as getter yielded a similar rate, suggesting this is determined primarily by the mixing rate. (3) For high level additions, the absorption rate decreases by a factor of about 2. (4) After large additions, it

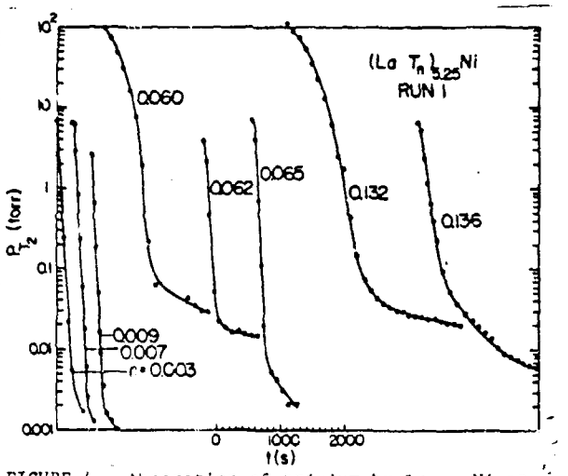

FIGURE 4. Absorption of tritium by $La_{5.25}Ni$ at 600°C.

takes a while for the alloy to recover and approaches to equilibrium are slow.

A second run was made under similar conditions except the temperature of the sample was varied between 550 and 650°C. There was no detectable change in absorption rate, although the final equilibrium pressure increased with temperature as expected.

Limited experiments were also done using low concentrations and counting techniques. For these, low concentration gas (1 ppm tritium in helium) was circulated over the alloy at 600°C. Over periods of about one h the tritium was gettered to a third or less of this value. Additions of larger amounts of tritium (1%) were rapidly absorbed but the tritium was only gettered down to the 10- to 100-ppm range. These experiments suggested that at low levels, apparent gettering rates are determined by adsorption on, and release from, the internal surfaces of the apparatus.

CONCLUSIONS

These experiments indicate that liquid eutectic alloys form stable, low-equilibrium pressure, hydrides. The absorption experiments indicate that $La_{5.25}Ni$ at temperatures near 600°C rapidly, and essentially quantitatively, getters tritium from helium streams to levels on the order of 10 ppm, and over periods of 1/2 h, to levels below 0.1 ppm. Thus this alloy, or others similar, should prove usable as getters in CTRs. Two major questions remain to be examined: what conditions are needed to reverse the cycle (drive off the gas) and what are the effects of impurities on the getter? Tritium experiments along these lines are continuing.

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